

On Oxidation and Adhesion of Copper-Filled PE

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ABSTRACT: The IR-spectroscopy and MVCIR technique were used to study the role of technological factors (filler content, film thickness) in oxidation of polyethylene coatings filled with copper powder. It was learned that copper powder introduced into polyethylene reduces the ultimate level of oxidation of both the outer surface layer and deep-seated layers of the polymer; also, the layer thickness of the specimens oxidized at diffusion conditions was observed to be decreased. Besides, the oxidation gradient determined through the specimen thickness was decreased on increasing the filler content. For example, with copper concentration over 3 vol %, the ultimate level of oxidation within the polymer layer that undergoes diffusive oxidation remains unchanged. The filler exerts its influence on bonding of the coatings, first of all through variations in the oxidation level of the polymer layer bordering on the substrate. For example, at the filler concentration above 3 vol %, the achievable level of adhesional strength does not depend on the coat thickness (the coat thickness being smaller than that of the diffusively oxidized layer). In thicker coatings, oxidative transformations do not, in fact, take place in the zone of adhesional contact, and the adhesion strength remains unchanged during thermal treatment. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2047–2052, 2001

Key words: polyethylene; copper powder; filler concentration; film thickness; oxidation level of polymer; distribution of oxidation products; adhesion strength of coating

INTRODUCTION

Most of our works dealing with oxidation of polyethylene in contact with copper studied oxidation of polyethylene films on copper substrates.^{1–6} Catalysis of oxidation in thin films (kinetic conditions of oxidation) was brought out as being due to transfer (accumulation) of copper-containing compounds in the polymer bulk.² *Copper transfer into oxidizable polyethylene was later proved by other scientists.*⁷ It was learned that transferred compounds were, in the most, copper carboxylates in hydrated or anhydrous state.^{8,9} A critical concen-

tration of copper-containing compounds is of dual nature.^{2,6}

When thick polyethylene films are oxidized on copper (diffusive conditions of oxidation) the catalysis of the substrate shows, first of all, in accelerated oxidation of the polymer in the zone of adhesional contact. The outer layer of the films is not actually oxidized during this period. However, the copper compounds transferred in the coating bulk gradually stimulate the oxidation process in the outer surface layer of the polymer. The oxidation developing in this layer restricts supply of oxygen to the zone of adhesional contact; as a result, oxidation transformations and migration of the metal within the layer, bordering on the substrate, becomes decelerated. Localization of oxidation in the surface layer leads to a large quantity of low molecular weight products of oxidation, among them such compounds as fatty ac-

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ids are present. Possessing high diffusive permeabilities, these compounds migrate into the coating bulk, including the zone of adhesional contact. As a result, a second stage of accumulation of oxidation products and copper-containing compounds begins in the polymer layer bordering on the substrate.¹⁰

These features of contact oxidation of polyethylene on copper substrates can show in polyethylene filled with dispersed copper. It should be noted that oxidation of filled polyethylene has not been studied systematically, and the available experimental findings were published in different papers.¹¹⁻¹³ The problem of distribution of oxidation products throughout the film thickness, when copper was the filler, has not been investigated, as well as adhesional properties of such films, and some other problems. In view of this, and also the opportunity of achieving the inhibiting effect in copper-filled polyethylene, we have done this research.

EXPERIMENTAL

Materials and Test Specimens

The following materials were used to prepare test specimens: powdered unstabilized polyethylene with molecular weight between 150,000 and 200,000 and fineness up to 250 μm (Grade 21006-075, GOST 16338-70, Russia), and powdered copper of fineness between 50 and 75 μm , Grade M1, Russia. To modify the polymer (PE), antioxidant 2,2-bis-[1-oxy-4-methyl-6-(α -methyl benzyl)-monosulphide] (thioalcofene MBP, VTU 7-63, Russia) was used.

Powdered PE and copper were blended to make compositions. PE and the modifiers were used to prepare blends. PE powder was mixed with copper powder to obtain a uniform composition. To prepare compositions of PE with the antioxidant, PE powder was placed into the solution of the antioxidant in acetone, then the solvent, i.e., acetone, was removed by evaporation at room temperature. PE powder and the compositions of PE with modifiers were used to prepare films of required thicknesses by molding at 150°C. Thus, prepared films were oxidized in air on substrates possessing different activities, namely on copper (Grade M1, GOST 5638-51, Russia), on aluminum (Grade A 99, GOST 618-62, Russia), and on window glass. The oxidized films were then separated from the substrate and tested. To estimate the distribution of oxidation products through the

thickness, sections 50- μm thick were cut from the film parallel to the outer surface.

Procedure

The oxidation level of the polymer was estimated from IR-transmission spectra, and multiply violated complete internal reflection (MVCIR) spectra. The optical density of the 1720 cm^{-1} absorption band in IR spectra was used to characterize the level of oxidation.¹⁴ The optical density was estimated by the baseline method. The optical density estimated from the transmission spectra, was recalculated for the 100- μm film thickness. The transmission and MVCIR spectra were recorded using UR-20 spectrophotometer (Karl Zeiss, Jena, Germany). When MVCIR spectra were recorded, an attachment with KRS-5 component was used ($\theta = 45^\circ$; $n = 2.4$; $N = 14$). The layer thickness of polyethylene subjected to examination did not exceed 3 μm in this case.

To estimate the oxidation effect of polyethylene on its crystallinity, thermograms of the films [curves of the differential thermal analysis (DTA)] were recorded using the differential scanning microcalorimeter DSM-2 (the test specimens were heated at the rate of 25°C/min). The degree of crystallinity of the polymer was described by the area under the endothermal peak of melting on the thermograms of the specimen expressing it in relative units, namely, the ratio of peak area to weight of the specimen (m^2/kg).

Also, the adhesion strength (adhesion bonding) of the polymer to the substrate was estimated. It was defined by resistance to peeling either of foil (aluminum and copper) from the coating film, or of coating from the substrate (glass). The rate of separation was 0.3 mm/s.

RESULTS AND DISCUSSION

Effect of Copper on Oxidation of Films

Figure 1 shows kinetic relationships for accumulation of carbonyl groups in thin polyethylene films (100 μm thick), containing different quantities of copper (curves 2 and 3). The plots of accumulation of carbonyl groups in unfilled coatings on copper substrate [1 and 3] are similar in appearance. During the initial period of thermal treatment the filler promotes the oxidation process; but with time, deceleration occurs and finally it ceases completely. The higher the filler concentration in the film, the higher the rate of

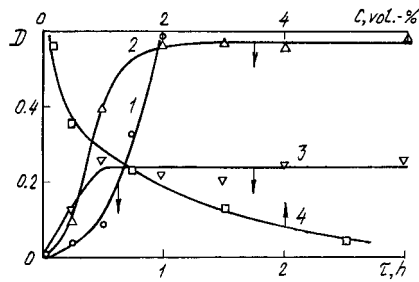


Figure 1 Oxidation level vs. time of thermal treatment on aluminum of unfilled PE (1) and PE filled with 0.2 vol % (2) and 1.5 vol % (3) of copper. (4) Ultimate oxidation level vs. copper content. Film thickness 100 μm . Temperature of thermal treatment 160°C.

catalyzed oxidation, and the earlier the inhibition stage occurs. On increasing the filler concentration, the ultimate oxidation level in the films decreases (Fig. 1, curve 4). This similarity in behavior of copper-filled and unfilled PE films on copper is explained by the fact, that on increasing the filler concentration, the thickness of the polymer interlayer that surrounds the filler particles decreases. It was learned earlier¹¹ that on decreasing the thickness of PE films, oxidized on copper substrate, the rate of oxidation of the polymer increased, the inhibition stage occurred earlier, whereas the ultimate oxidation level decreased. Thus, in its effect on PE oxidation, the decreases in thickness of unfilled films on copper are equivalent to the increases in copper filler concentration in the films, that is, there is a reverse analogy (dependence) between the film thickness and filler concentration.

The data shown in Figure 1 represent an averaged oxidation level of the films. Assuming a non-uniform propagation (development) of the oxidation process through the specimen thickness, the MVCIR procedure was used to learn the accumulation of carbonyl groups in the surface layer of copper filled PE. The results are shown in Figure 2. The filler influences oxidation of the surface layer in the manner similar to that of the film bulk. The higher the filler concentration, the quicker the polymer oxidizes at the initial stage, the earlier the ultimate oxidation level is achieved, and the lower its value (Fig. 2, curves 2, 3, and 4).

The high activity of the copper filler at the initial oxidation stage can be supported by the data on variations of the induction period of oxidation. On increasing the filler concentration, the duration of the induction period of oxidation decreases, as it was estimated from the MVCIR

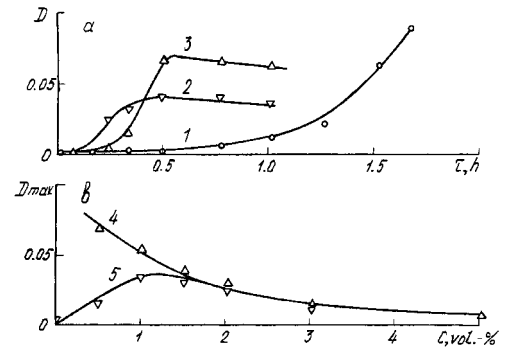


Figure 2 (a) Oxidation level of surface layer in PE films: (1) unfilled; (3) filled with 0.5 vol % copper; (2) 1.5 vol % of copper vs. time of their thermal treatment on aluminum. (b) Ultimate (4) and current (time of thermal treatment 20 min) (5) oxidation levels of surface layer in PE films vs. copper content. Film thickness 300 μm . Temperature of thermal treatment 150°C. Data were obtained using MVCIR technique.

spectra of the surface layer of the specimens (Fig. 3, curve 3).

In addition to MVCIR data on variations of the ultimate oxidation level. Figure 2 shows relationship of the current oxidation level (short thermal treatment) vs. filler concentration (curve 5). This relationship, as well as the relationship between the copper concentration and rate of oxidation,¹¹ has a peak. The growth in oxidation level (up to the maximum) can be explained by higher rates of polymer oxidation on increasing the filler copper concentration. The maximum corresponds to the copper concentration at which, at a given duration of thermal treatment, the kinetic curve of accumulation of carbonyl groups reaches the stage of inhibition. At higher filler concentrations,

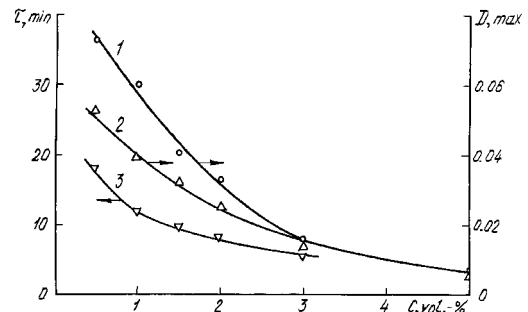


Figure 3 Ultimate level of oxidation (1 and 2) and induction period of oxidation (3) for outer surface layer (1 and 3) and for layer seated at 50 μm from the surface (2) of PE films vs. copper content. Film thickness 300 μm ; temperature of thermal treatment 150°C. Data were obtained using MVCIR technique.

Table I Variations in Area under Melting Peak ($\times 10^{-2} \text{ m}^2/\text{kg}$) for PE Films Oxidized at 150°C

Specimen	Duration of Oxidation, hour							
	0	0.25	0.5	0.75	1	2	3	5
PE on glass	4.58	4.46	4.32	4.77	4.46	4.19	3.45	2.65
PE filled with copper 0.5 vol % (on glass)	4.55	4.49		4.75	4.35	4.53		3.96

curve 5 in Figure 2 represents the respective section (region) of curve 4 (Fig. 2), which shows variations in the ultimate values of oxidation level vs. filler concentrations. On increasing the duration of thermal treatment, the peak on the plot (Fig. 5, curve 5) shifts to the region of lower filler concentrations.

The MVCIR data indicated that at the inhibition stage of oxidation of the surface layer of the film the amount of carbonyl groups in it somewhat decreased (Fig. 2, curves 2 and 3). This shows especially clear in decreased integral intensity of the absorption band at 1700–1800 cm^{-1} . The integral intensity was described by the area of the absorption band.¹³ *In our opinion*, decreased concentrations of carbonyl groups in the surface layer of the film can be explained by evaporation of low molecular weight products of oxidation as well as by their diffusion into the deeper layers of the specimen.

The oxidation transformations in copper-filled PE occurred mainly within imperfect regions of the specimen, which formed an amorphous interlayer after the polymer was cooled and crystallized. This is explained by the fact that the degree of crystallinity in the filled PE (the area under the melting peak on the thermograms) varies negligibly after oxidation, compared with the unfilled polymer (Table I). Probably, copper compounds are transferred along these imperfect regions in the specimens. As a result, the polymer becomes a *particular* composite material in which the inhibited amorphous polymer is the matrix, and the crystallized material is the filler.

Distribution of Oxidation Products in Filled PE Films

The distribution of oxidation products through the specimen thickness is shown in Figure 4. In unfilled polyethylene the surface layer (up to 100 μm thick) becomes deeply oxidized; therefore, it is impossible to determine the optical density of the absorption band at 1720 cm^{-1} from the IR-transmission spectra, (Fig. 4, curve 1). In the remain-

ing part of the specimen, the carbonyl groups are distributed in the exponentially decreasing manner. In copper-filled PE specimens, the surface layer appears less oxidized; therefore, the oxidation level can be estimated through the whole thickness of the specimen (Fig. 4, curves 2, 3, and 4). It was learned that on increasing the filler concentration, the ultimate values of optical density decreased in both the surface layer and deeper seated layer of the coating. Therefore, if the total oxidation level of a specimen is described by the area of the figure confined by the coordinate axes and by the corresponding curve in Figure 4(a), one can assume that the higher the filler concentration in the PE film, the lower its total level of oxidation. At relatively low copper contents (e.g., 5 vol %), a mean extinction index (through the film thickness) of the absorption band at 1720 cm^{-1} was 4 cm^{-1} (under the term "extinction index" we understand the ratio of optical density of the band to the film thickness expressed in cm). Therefore, inhibited copper-filled polyethylene films can be of interest for those engaged in developing novel materials. On increasing the filler concentration, the gradient of

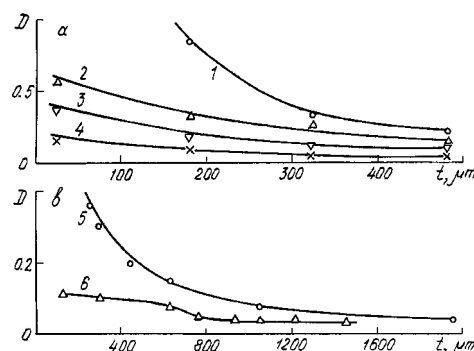


Figure 4 Distribution of ultimate oxidation level through PE film thickness: 500 μm (a) and 200 μm (b) on aluminum substrates. Unfilled films (1 and 5), PE films filled with copper: (2) 0.2 vol %; (3) 0.5 vol %; (4) 1 vol %; (5) 1.5 vol %. Thermal treatment was run at 150°C.

oxidation level of the polymer decreases through the film thickness. Figure 3 shows, for comparison, concentration dependencies of the ultimate oxidation level (MVCIR data) for the surface layer of the specimen (curve 1) and the layer seated at a 50- μm depth from the surface (curve 2). At filler concentrations between zero and 3 vol %, the surface layer is oxidized more severely than the deeply seated layer; at higher contents of copper the relationships coincide. This fact indicates that approximately equal oxidation levels characterize the polymer through the film thickness.

This situation can be explained as follows. At low filler concentrations (the polymer interlayer is thick between filler particles) the oxidation of films resembles, in many aspects, the oxidation of unfilled films on copper substrate. Oxidation starts first in the layer bordering on the metal (filler particles). A considerable part of the polymer interlayer remains unoxidized. As oxidation continues, more oxygen is consumed (absorbed), and the oxidation process shifts gradually to the outer surface layer of the film. At this stage, the remaining part of the polymer interlayer becomes oxidized and the whole interlayer gets saturated with copper compounds. Thus, a two-step regime of oxidation and metal transfer works in polymer interlayers. The relationship (the plot) of distribution of oxidation products through the film thickness is of decreasing nature in this case. On increasing the filler concentration the thickness of polymer interlayer decreases. We had learned earlier¹¹ that with decreasing the film thickness the ultimate oxidation level decreases for the polymer being in contact with the copper sub-

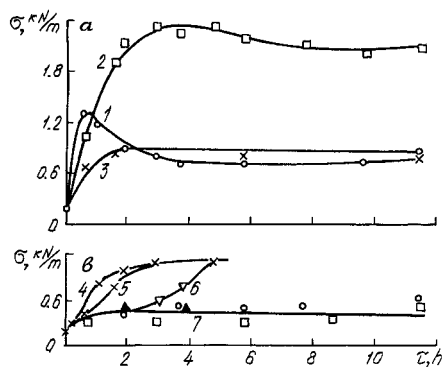


Figure 5 Adhesion of PE to aluminum vs. time of thermal treatment for coatings of thickness 300 μm (1 and 4); 500 μm (5); 800 μm (6); 1200 μm (2 and 7, \blacktriangle); 2000 μm (3 and 7, \circ), and 3000 μm (7, \square). Unfilled PE (1, 2, and 3). PE + 5 vol % copper (4, 5, 6, and 7). Temperature of thermal treatment 150°C.

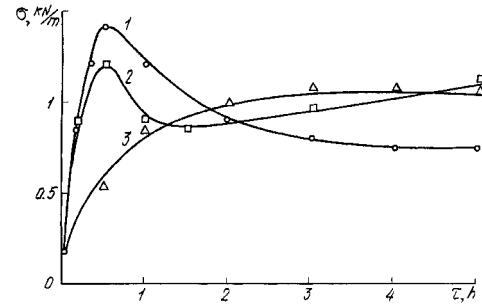


Figure 6 Adhesion of PE to aluminum vs. time of thermal treatment for coatings of 300 μm thick: unfilled PE (1); PE + 0.5 vol % copper (2) and PE + 5 vol % copper (3). Temperature of thermal treatment 150°C.

strate, that is a lower amount of oxygen is required to oxidize it. At higher filler concentrations (over 3 vol %) the consumption of oxygen reduces to such an amount that the film's permeability is quite adequate to ensure oxidation of the whole polymer material at the one-step regime. In this case, oxidation is not forced (shifted) to the outer surface layer and the oxidation levels are equal through the thickness of the polymer layer oxidized at diffusion conditions.

The plot of distribution of oxidation products in copper-filled PE films (copper concentration 1.5 vol %) has a sharp line that divides the specimen into two parts, each having a different oxidation level (Fig. 4, curve 6). In the outer (upper), most oxidized, part of the specimen, oxidation proceeds at diffusion conditions, while the lower (bordering on substrate) part of the specimen remains, in fact, unoxidized. In filled polymer, the thickness of diffusively oxidized layers is much less than that in unfilled polymer (0.8 and 1.6 mm, respectively). The part of the specimen bordering on the substrate also contains oxidation products (optical density between 0.04 and 0.05), but it is mainly the result of low molecular weight products migrated from the upper oxidized part.

Effect of Copper on Adhesion of Films

Figures 5 and 6 show data on adhesion of polyethylene films to substrates having different activities. Adhesion values of unfilled PE films to aluminum vs. oxidation period reach a maximum, after which they decrease to some constant level, (Fig. 5, curves 1 and 2). The adhesion values begin to increase from this level with increasing the film thickness. The time, required for the kinetic dependences of adhesion to reach the stabilization region, corresponds to the time required

for the kinetic dependences of oxidation level (of PE in the layer bordering on the substrate) to reach the stabilization region.¹⁵ As the adhesives (*adhesive joints*) broke down along the polymer layer, after a maximum in adhesion was reached (polymer remnants can be visualized on the metallic substrate surface), it is thought that stabilization of adhesion between PE and aluminum is associated with termination of PE oxidation in the polymer layer bordering on the substrate. On increasing the film thickness from 1300 to 1600 μm , the maximum values of adhesion decreased, whereas the plot of adhesion vs. oxidation period (of films on substrates) resembles the curve that reaches a stable level. Beginning from 1600 μm , absolute values of adhesion are independent of the film thickness, i.e., they fall onto one curve, (Fig. 5, curve 3). Evidently this thickness is a limiting depth of the layer that oxidizes diffusively. In the case of films, the thickness of which is above 1600 μm , the polymer layer bordering on the substrate is not oxidized, in fact, and thermal treatment of the coating in an oxidizing environment does not affect adhesion strength. The presence of copper in PE causes the maximum on the adhesion plot to degenerate at smaller thicknesses of the film. At higher filler concentrations, the kinetic dependence of adhesion is a curve with saturation, i.e., the curve reaches a stable level (Fig. 6, curves 1, 2, and 3).

Figure 5 compares data on variations of adhesion for PE films of different thickness, containing 5 vol % of copper. The adhesion of coatings oxidized at diffusion conditions and treated thermally reaches a steady value (about 1 kN/m); here, the thicker the coating, the longer thermal treatment is required (Fig. 5, curves 4, 5, and 6). The constant values of adhesion for films of different thicknesses is explained by the fact that at filler contents over 3 vol % the oxidation levels of the polymer in deep-seated layers of the polymer film are identical. Because of the diffusive nature of polymer oxidation, the rate and accordingly the oxidation level are the lower the deeper the layer under examination is seated; the duration of thermal treatment being the same. Therefore, the time required to achieve steady oxidation level in the polymer layer bordering on the substrate is the longer, the thicker the film thickness. Accordingly, the thicker the film, the longer the time required to achieve ultimate values of adhesion.

In coatings of thicknesses that exceed the thickness of the layer oxidized at diffusive condi-

tions, no oxidation transformations take place in the polymer within the adhesional contact zone, and thermal treatment does not affect adhesion (Fig. 5, curve 7).

In conclusion, the addition of copper powder to polyethylene reduces the ultimate level of oxidation of both outer surface and deeper seated polymer layers; the thickness of the layer oxidized at diffusive conditions also gets reduced. The added copper influences adhesion of PE, mainly through variations in the oxidation level of the polymer layer bordering on the substrate.

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